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SCHENECTADY, NEW YORK

IMMOBILIZED LIQUID MEMBRANES FOR SULFUR DIOXIDE SEPARATION

FINAL REPORT

Contract No. PH-86-68-76

Prepared for

Department of Health, Education, and Welfare
U.S. Public Health Service
'National Air Pollution Control Administration
5710 Wooster Pike
Cincinnati, Ohio 45227

W.J. Ward III and C.K. Neulander
General Electric Research and Development Center
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S-70-1053

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ABSTRACT

An immobilized liquid membrane has been developed which at 100°C has an SO_2 flux of

$$3.2 \times 10^{-3} \frac{\text{cc (STP)}}{\text{sec, cm}^2\text{, cm Hg } \Delta P}$$

and an SO_2/CO_2 separation factor of 14. The membrane operated for one month at 100°C with no change in permeation properties. The membrane could not withstand a pressure difference of 1 atm across it. However, a technique was recently developed which may make it possible to overcome this limitation.

The low SO_2/CO_2 separation factor makes the use of this membrane for removing SO_2 from power plant stack gases economically unattractive. An economically attractive system has been conceived for treatment of higher SO_2 concentration, and lower total flow stack gases, such as those emitted from many ore-smelting processes.

IMMOBILIZED LIQUID MEMBRANES FOR SULFUR DIOXIDE SEPARATION*

W. J. Ward III and C. K. Neulander

INTRODUCTION

Today, sulfur oxide pollution is a substantial threat to people and agriculture in many areas of the world. With present control practices the rate of SO_2 discharge in the United States will double by 1980. Past research efforts on means of controlling SO_2 pollution have concentrated on methods for removing SO_2 from combustion gases and extracting sulfur from coal and residual oil. Sulfur dioxide elimination from combustion gases has been the subject of more research than any other gas purification operation, but the results have not been satisfactory. Much of the past and present research has centered around the identification of the nature and magnitude of the problem. While this has been useful, what are clearly needed are methods of control. Several first generation processes currently under development may be economically tolerable in certain critical areas. However, entirely new approaches to the problem must be developed if problems beyond the 1975 to 1980 period are to be met. The following is a report on the initial developmental work on one such approach.

Over the years there have been many attempts to develop semipermeable membranes for separation processes, and patents on potential processes date back more than a century. However, it is only in the past 10 years that membranes have been developed which make certain membrane separation processes within range of being economically and technically feasible. Although several polymers such as silicone rubber and cellulose acetate are useful membrane materials, in general, polymeric materials are not desirable as semipermeable membranes since most are relatively impermeable to all gases and liquids. Several years ago, W. L. Robb[1] considered liquids as potential membrane materials, and based on this concept a highly effective immobilized liquid membrane for CO_2 removal from a life-supporting environment was developed by Ward and Robb.[2]

The transfer of a solute through polymeric and liquid membranes occurs by a solution/diffusion mechanism. That is, the solute dissolves in the membrane, diffuses through it, and desorbs on the other side. The permeability of a nonreacting solute in a membrane is thus the product of the diffusion coefficient and the solubility of the solute in the membrane. A standard set of units for permeability, which is consistent with this definition, is

$$\frac{\text{cc(STP), cm thickness}}{\text{sec, cm}^2\text{, cm Hg } \Delta P}\ .$$

In the case of gas permeation, the driving force for the transfer of a gas through a membrane is a partial pressure difference in that gas across the membrane. In the case of SO_2 removal from stack gases, there are only two reasonable ways of maintaining a partial pressure difference in SO_2. One is to evacuate one side of the membrane, and the other is to sweep away with a condensable gas the SO_2 permeating through the membrane. A combination of these two methods is also possible.

Liquids are under consideration here as membrane materials since they have large diffusion coefficients compared to polymers; and also, for certain gases, they can have enormous solubilities. Thus liquids can be highly permeable to, and highly selective for, certain gases, particularly polar ones such as SO_2. Liquid membranes can be made in a variety of ways. Very stiff gels can be used as membranes. In some cases a polymer membrane can be swelled with a liquid to the extent that the liquid controls the rate of permeation. In some cases a high-grade microporous filter can be impregnated with the liquid, and this will serve as the liquid membrane. In the present work, fabricating the liquid membrane was particularly difficult because it had to be very thin.

In general, packaging membranes in the form of usable hardware is a formidable problem which only recently is receiving intensive consideration. The design and fabrication of membrane packages was not within the scope of this work. However, immobilized liquid membrane packages are being made in this Laboratory, and from this work it can be assumed that packaging densities of the order of 100 to 500 square feet of active membrane area per cubic foot of volume can be achieved.

The present investigation was concerned with developing an immobilized liquid membrane which was highly permeable to and selective for SO_2 at elevated temperatures, and devising an appropriate membrane system for removal of SO_2 from stack gases.

MEMBRANE DEVELOPMENT

Membrane development included selection of the optimum membrane liquid and fabrication of an immobilized film of this liquid. The primary requirements of the membrane were:

1. The SO_2 flux must be of the order of

$$4 \times 10^{-3}\ \frac{\text{cc(STP)}}{\text{sec, cm}^2\text{, cm Hg } \Delta P}\ .$$

Thus for a liquid film 1 mil thick, the SO_2 permeability must be

$$10,000 \times 10^{-9} \frac{\text{cc(STP), cm}}{\text{sec. cm}^2\text{, cm Hg } \Delta P}$$ *

As a point of comparison, silicone rubber, one of the most permeable membrane materials, has an SO_2 permeability at 25° and 100°C of

$$1500 \times 10^{-9} \text{ and } 750 \times 10^{-9} \frac{\text{cc(STP), cm}}{\text{sec, cm}^2\text{, cm Hg } \Delta P},$$

respectively. The membrane must also be highly selective for SO_2. In order that it have application for SO_2 removal from combustion gases, which typically contain of the order of 0.2% SO_2, the SO_2/CO_2 separation factor (ratio of SO_2-to-CO_2 permeability) of the membrane would have to be of the order of several hundred. Oxygen and nitrogen permeabilities are not a problem since they would be at least 10 times less than CO_2. For the membrane to have application for more concentrated stack gases such as 2% to 10% SO_2 which might be produced in a smelter, the SO_2/CO_2 separation factor would have to be at least 10. Silicone rubber has SO_2/CO_2 separation factors at 25° and 100°C of 5 and 2.5, respectively.

2. The membrane must be able to operate at elevated temperature. In this work an operating temperature of at least 100°C has been the goal.

3. The membrane liquid must be chemically inert and nonvolatile at the operating temperature.

4. The membrane must have an effective life of at least one year and perhaps more.

When the diffusion coefficient (D) of a permeant is independent of concentration and time, and when the solubility (S) follows Henry's law, the following relation obtains

$$Pr = (D)(S) \quad . \qquad (1)$$

This equation holds well enough to serve as a guide in selecting suitable liquids for the gas separation desired here. Since the diffusion coefficient is of the order of 10^{-5} cm^2/sec for most solutes in most liquids, one is primarily concerned with finding liquids with high SO_2 solubilities and low CO_2 solubilities. Table I is a summary of the solubility data obtained on what were considered to be the most promising membrane liquids. Besides being polar, all of the liquids were chemically inert and nonvolatile at 100°C.

From Table I it is seen that the polyethylene glycols (PEG) have the highest SO_2 solubility of all the liquids tested. Thus this material was more thoroughly characterized. The solubility of CO_2 and SO_2 in Union Carbide Carbowax 600 polyethylene glycol was measured from 75° to 150°C, and the results are shown in Fig. 1. The solubility of N_2 and NO at 100°C were found to be 3.2×10^{-3} and 4.8×10^{-3} moles/ℓ, respectively, at 1 atm of gas over the solution. It is clear from these data that at 100°C a film of PEG is sufficiently selective for SO_2 to be useful in treating stack gases having of the order of 5% SO_2, but is not suitable for very dilute stack gases.

It was found that at 100°C oxygen reacted with the PEG although the rate of attack was substantially reduced by excluding light. If it is assumed that for each mole of oxygen consumed a mole of PEG is destroyed as a useful membrane material, then the rate of degradation was 0.23% per day. This rate was insensitive to the oxygen pressure over the solution in the range of 10 to 40 mm Hg. Various antioxidants were added to the solution. The most effective was Ionox-330 (Shell Chemical Co.) at 0.2%, which decreased the oxidation rate to 0.16% per day. Thus it appears that oxygen degradation is not a serious problem.

Assuming a diffusivity for SO_2 of 1×10^{-5}, the permeability of SO_2 in PEG is 2.95×10^{-6} at 100°C. Based on the flux requirements for SO_2 stated above, in order to have an acceptable throughput for SO_2 a film of pure PEG would have to be approximately 8μ thick. Immobilizing the PEG will lower the SO_2 diffusivity by a factor of 2 to 3, and it can be reasonably assumed that an immobilized film must be less than 3μ thick for it to be of practical value.

The first task in fabricating a membrane of PEG was to find a material that would thicken or gel it. Numerous water-soluble polymers were tested, but none was suitable. It was found that a 5% solution of hydroxymethyl cellulose (HMC), marketed as Cellosize by Union Carbide, would not dissolve in PEG, but that a film cast from an aqueous solution of Cellosize and PEG was clear and reasonably strong. The HMC film was swollen with PEG, and the PEG not in the polymer matrix simply adhered to the swollen polymer film. The permeability of films containing 90% PEG and 10% HMC was determined. The films were backed by a 1-mil silicone rubber membrane to avoid forcing the liquid out of the polymer matrix when a pressure difference was applied. The resistance of the silicone rubber membrane to nitrogen and carbon dioxide permeation was known, and it was small compared to the resistance of the PEG film. The composite film was supported on a porous stainless steel disk and the permeation measurements were made in a vacuum system with a pressure difference of 1 atm across the film. The permeability was determined by allowing the gas passing through the film to build up a pressure in the vacuum system of approximately 500μ Hg over a measured time interval. At room temperature and 100°C the following data were obtained:

	25°C	100°C
Permeability of CO_2	17×10^{-9}	56×10^{-9}
CO_2/N_2 separation factor	48	≈ 15
Calculated diffusivity of CO_2	7×10^{-7}	5×10^{-6}

*These units are used throughout.

TABLE I

Survey of Potential Membrane Materials

Liquid or Solution Tested	Temp. (°C)	SO_2 Solubility mol/ℓ at 1 atm SO_2	Comments
1. Carbowax 600 (Polyethylene glycol)	100	0.766	
	80	1.26	
2. Carbowax 4000 (PEG)	100	0.697	
3. Diphenyl sulfoxide	100	.656	
4. Two aromatic hydrocarbons made by GE on laboratory scale			
#1	100	.425	
#2	100	.195	
5. Versamide #115, polyamide made by General Mills			Solution decomposed when contacted with SO_2, 100°
6. 5% solution of silicone stopcock grease in 6-ring polyphenyl ether	100	.158	
7. Dioctyl phthalate	100	.246	
8. 20 gms phenyl sulfone in 24 cc of tricresol phosphate	100	.328	
9. Phenyl sulfone	135	--	Very low SO_2 solubility
10. 2 gms benzene sulfonamide in 10 cc tricresol phosphate	100	.298	
11. 2 gms sulfanilamide in 10 cc Carbowax 400 (PEG)	100	.595	
12. 10 gms sulfanilamide in 10 cc Carbowax 400 (PEG)	100	0.356	
13. 1 gm saccharin in 10 cc Carbowax 400 (PEG)	100	--	Solution unstable
14. 3 gms nicotinamide in 10 cc Carbowax 600 (PEG)	80	1.26	
15. 20 gms polyethyleneimine in 10 cc Carbowax 600 (PEG)	100	--	SO_2 reacted with solution giving H_2S
16. Polyphenyl ether (Monsanto OS 138)	100	0.18	
	75	.29	
17. Dow Corning 704 Diffusion Pump Fluid	100	.17	
18. GE Aromatic hydrocarbon	100	.15	
19. Tricresol phosphate	100	.37	
20. Uvinul N-539 (GAF)	100	.25	

Thus at room temperature the PEG/HMC film was quite impermeable, but at 100°C it approached the permeability of pure PEG. It was concluded that a suitable film could be made from the PEG-HMC combination.

Obviously it was necessary to have a mechanical support for the liquid film. It was found that a non-wetting porous backing could be made by depositing a microporous layer of Teflon on a porous support. A colloidal dispersion of 0.25μ Teflon particles was sprayed onto a 75μ thick Solvinert[3] membrane having 0.25μ pores. The Solvinert film was attached to a hot plate set at 150°C. A Teflon layer approximately 25μ thick was deposited. After spraying, the composite Teflon-Solvinert film was heated in air at 200°C for approximately 1/2 hour. This temperature was sufficient to drive the wetting agent (Triton X-100)

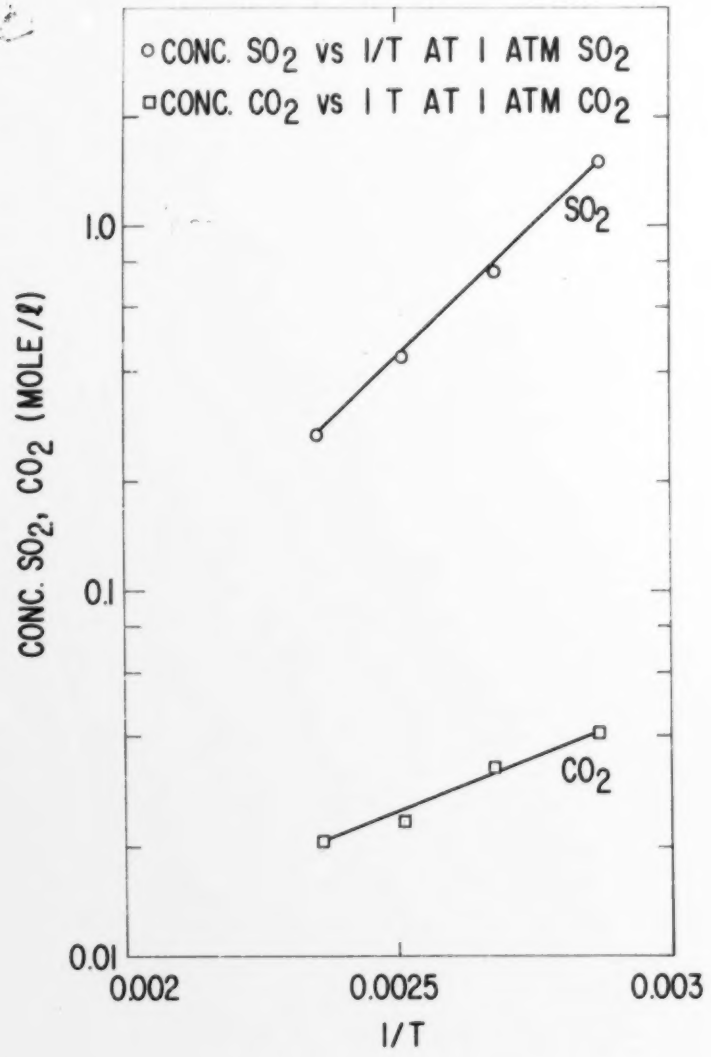


Fig. 1 SO_2, CO_2 solubility in polyethylene glycol.

out of the Teflon layer, making it nonwetting. This microporous Teflon film was completely nonwetting to PEG at 100°C for an indefinite time if there was no pressure difference across the PEG.

Clearly, if an immobilized PEG film 3μ thick was to be made, it would have to be formed directly on the Teflon support. This required that the surface of the Teflon be made wetting. It was found that this could be accomplished by spraying a very dilute PEG-HMC solution on the Teflon film. A suitable spraying solution consisted of

0.02% Cellosize QP-4400 (HMC)
0.6% Carbowax 600 (PEG)
99.4% Water

A loading of approximately 50 mg/cm^2 of spraying solution was sufficient to render the Teflon surface wetting. At this point there was not a continuous liquid film on the Teflon support. To form such a film, the wetting Teflon film was dipped into and withdrawn from a dilute aqueous solution of PEG and HMC. When the water evaporated, a continuous immobilized

TABLE II

Dipping Solutions Used to Form Immobilized PEG Films

Solution	cc of 1% Cellosize (QP-100M) Solution	H_2O (cm^3)	Carbowax (grams)
1	100	150	20g Carbowax 600
2	100	100	20g Carbowax 4000
3	100	125	20g Carbowax 4000
4	100	150	20g Carbowax 4000
5	100	200	20g Carbowax 600
6	100	250	20g Carbowax 4000

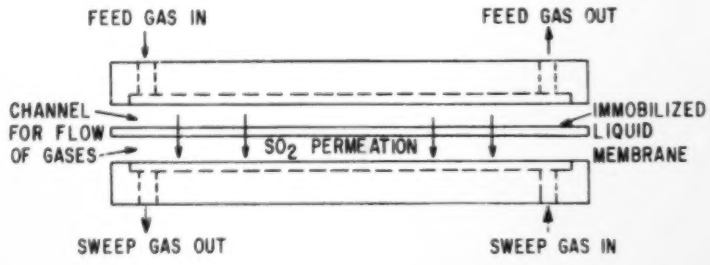


Fig. 2 Permeation cell used for testing immobilized liquid membranes.

film of PEG remained on the porous Teflon support. Six different aqueous PEG/HMC dipping solutions were used. These are listed in Table II.

Permeation measurements were made on the films produced from the solutions listed in Table II. The system shown in Fig. 2 was used. The SO_2 or CO_2 concentrations in the exiting feed and sweep gases were measured, and knowing the flow rates of each stream, the SO_2 or CO_2 flux was calculated. Results of these runs are presented in Table III. Solution #3 was found to be optimum. This gave a 3μ film which had constant permeation properties during a one-month life test (run #8, Table III). This is a remarkable performance for a liquid film 3μ thick.

The major limitation of this membrane is that when a pressure difference was applied across it, the backing was wetted and the film was destroyed. As discussed below, substantial advantages in the system could be gained if the membrane could be operated with a pressure difference. At the end of this program a method of accomplishing this was developed.* It was found that through the use of Cabosil, an extremely fine grade of silica marketed by Cabot Corporation, a film of polyethylene glycol could be sufficiently gelled so as to prevent wetting of two porous backing materials when pressure differences as high as 25 psi were applied at 100°C. Suitable backing materials were Millipore Solvinert and a porous polypropylene film sold by the Celanese Corporation.

*The work described below was done by Jerry Meldon, a summer employee of General Electric Research and Development Center, who is currently a graduate student at the Massachusetts Intitute of Technology.

TABLE III

Permeation Runs Made on PEG/HMC Films. All Runs at 100°C Unless Otherwise Noted.

Run	Dipping Soln. (Table II)	SO_2 Flux $\left[\frac{\text{cc (STP)}}{\text{sec, cm}^2\text{, cm Hg } \Delta P}\right]$	CO_2 Flux $\left[\frac{\text{cc (STP)}}{\text{sec, cm}^2\text{, cm Hg } \Delta P}\right]$	Comment
1	1	1.5×10^{-3} to 3.0×10^{-3}	--	Variable SO_2 flux due to variable mixing of 20-mil gas films adjacent to membrane. Filled gas flow channels with 20-mil screen for subsequent runs
2	5	4.3×10^{-3}	--	
3	6	3.7×10^{-3}	--	Proof that film could be made with Carbowax 4000
4	6	3.9×10^{-3}	1.5×10^{-3}	SO_2 fluxes at 70° and 100°C were equal. Low SO_2/CO_2 separation factor indicates film was not continuous
5	2	1.97×10^{-3} (100°C) 2.0×10^{-3} (70°C)	0.158×10^{-3} (100°C) 0.131×10^{-3} (70°C)	SO_2/CO_2 separation indicates continuous film was achieved. Films were probably not continuous in runs 1-3
6	4	--	--	No SO_2/CO_2 separation. Therefore solution #4 does not give continuous film
7	2	1.61×10^{-3} After 11 days 2.9×10^{-3}	0.123×10^{-3} After 11 days 0.51×10^{-3}	Flux changes with time. This was found to be due to seepage of oil from the constant temperature bath into the membrane backing. Cell was run in an oven in subsequent run
8	3	3.2×10^{-3}	0.22×10^{-3}	Film was run for 1 month with no change in fluxes

The procedure finally arrived at by Meldon for preparing the membranes is as follows:

1. 2.4 grams of Cabosil HS-5 were dispersed in 50 ml water in a blender at low speed for 2 minutes;

2. 12 grams of Carbowax (PEG) 4000 were dissolved in 80 ml water and blended into (1) at low speed for 1 minute; and

3. 2 grams of Cellosize (HEC) QP-100M were dissolved in 200 ml water and blended into (2) at low speed for 1 minute, followed by high speed for several seconds.

The resulting mixture was 0.7% Cabosil, 3.6% PEG, and 0.6% HEC, and the rest water.

A film of Cabosil, PEG, and HEC could be cast onto porous polypropylene or Solvinert by the following procedure:

> A sheet of backing membrane was taped onto a 1/8-inch copper plate on a hot plate at 80°C. A mixture containing half the above concentrations of Cabosil, HEC, and PEG was sprayed on, using an airbrush. When the water evaporated a gelled Carbowax film was left which was not continuous. A continuous film was then cast by dipping the sprayed membrane into the above concentrated mixture. The membrane was then allowed to dry in air.

The resulting film was approximately 1 mil thick. It displayed the same selectivity and permeability as

the films previously prepared with a Teflon/Solvinert substrate. Furthermore, whereas the films prepared previously without Cabosil wet the backing under a pressure difference of 1 atm, no wetting with the Cabosil-gelled films was found with pressure differences of 25 psi. Assuming the feasibility of casting thinner films which is reasonable but remains to be demonstrated, the required SO_2 flux could be achieved with this film.

SYSTEMS DEVELOPMENT

Concurrently with the development of a suitable membrane, the technical and economic feasibility of several SO_2-removal systems were studied. Various methods of providing the necessary driving force for efficient SO_2 permeation were investigated. These included removal of the SO_2 from the permeate side of the membrane by both physical and chemical means. The systems work also included a study of the possible by-products and processes which could be incorporated into the systems planning. Economic analyses were prepared on those concepts which appeared to be technically feasible, and rough attempts at systems optimizations were made. The calculations were often upgraded as new information was made available from the membrane research and development.

Economic analyses were based on equipment cost-estimating nomographs and data from several sources,[4-7] and were updated to 1967 utilizing Chemical Engineering Magazine's annual plant cost and equipment cost indices. Total plant cost figures were estimated by using an over-all multiplicative factor (of 4.0) on the total purchase price of the major pieces of equipment used in each process. Operating cost data included depreciation at the rate of 14% of fixed capital charges per year.

Several schemes can be conceived to maintain a low partial pressure of SO_2 on the back, permeate side of the membrane. Chemical means of removing the SO_2 would require a reactive sweep vapor to be employed. The reaction between the SO_2 and the reactive medium must be rapid, and, if the reaction product itself is not commercially attractive, it must be easily reversible. Many cases have been reported in the literature (see Appendix A) detailing the thermally reversible reactions between SO_2 and various unsaturated olefinic-type compounds. Most of the cases so described involved a liquid phase, catalyzed reaction within a tightly sealed pressure vessel, and resulted in a series of rather complex polymerization products (polysulfones). Reaction times were long (several hours) and yields were generally low. Two papers (Refs. A3 and A4 of Appendix A) describe the formation of sulfinic acids from sulfur dioxide and hydrocarbons (both olefins and paraffins) in the gas phase. However, the reaction takes place only in the presence of ultraviolet light, and again it was relatively slow. No information on the ease of thermal reversibility of these reaction products was given. Thus, because of the complicated chemistry, inapplicable system conditions, and relatively slow reaction rates required by the above reactions, it was decided to rule out this scheme for removing SO_2 from the back side of the membrane.

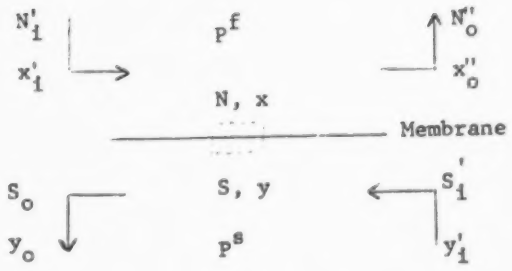
Physical methods of doing this include diluting and sweeping the permeating gases from the back surface of the membrane with another gas or vapor, maintaining the back side of the membrane under vacuum, or a combination of the above two, i.e., using a sweeping medium at subatmospheric pressures. Major equipment requirements for the above methods include boilers and condensers if a condensable vapor is used as the sweep medium, and gas compressors and associated vacuum equipment if subatmospheric pressures are involved. Additional equipment would be required depending on the recovered final product. Since the driving force for permeation for a given component is a difference in partial pressure across the membrane, operating at reduced pressure on the sweep side would enable a more concentrated SO_2 gas to be collected (for a constant total volumetric flow). Also, the mass of sweep gas required for a given separation would be lower, which becomes an important consideration if a condensable vapor is used for the sweeping stream. In this case, the SO_2-containing sweep stream may be concentrated still further by condensing the vapor. Obviously, additional effort must be expended to compress and recover these off-gases.

System analyses soon indicated that a swept system would be most feasible, both technically and economically (see below). Thus, a computer program was assembled to enable rapid calculation of membrane area and feed and sweep gas compositions and flow rates. The program used as a model a countercurrent, plug flow operating system (see Fig. 3). Input data included initial feed and sweep flow rates and compositions, an estimated feed exit flow rate and composition, operating pressures, and the desired reduction of SO_2 concentration in the feed gas stream. A five-component gas stream was considered (SO_2, CO_2, H_2O, O_2, N_2). Based on the experimentally determined (or estimated) permeabilities of these compounds in the membrane, the flux of each component was calculated over an area increment small relative to the total area required for the given separation. The mathematical equations required for the calculations were based on two relations: one describing the flux of any component across a differential area element by the definition of permeability [Eq. (2)], the second being a mass balance about the incremental area element [Eq. (3)],

$$N \frac{dx}{dA} = \frac{Pr}{\delta} (P^f x - P^s y) \qquad (2)$$

$$N (x - x_0) = S (y - y_i) \ . \qquad (3)$$

An assumption was made [included in Eqs. (2) and (3)] that the total gas flow rate (both feed and sweep) was constant over a single area increment. This was justifiable by the use of a small area increment and



Nomenclature

N - Feed flow rate (at standard conditions)
S - Sweep flow rate (at standard conditions)
x - Feed component concentration
y - Sweep component concentration
P - Operating pressure

Subscripts:

i - initial (inlet) value
o - final (outlet)value

Superscript:

f - feed side condition
s - sweep side condition
' - known value
'' - assumed value

Fig. 3 Model for membrane area calculation.

by the fact that the major portion of the feed gas streams under consideration was composed of essentially impermeable components.

Equation (3) was used to describe the sweep concentration (y) as a function of feed concentration (x) and known constants (x_0, y_i, N, S). This relation was incorporated into Eq. (2), which could then be integrated in closed form to enable the calculation of a pseudo-feed concentration for each component over the area increment. The flux of each component was calculated, from which the total flow rate and gas composition were recalculated at the interior point. The calculation was continued automatically until the feed SO_2 concentration equaled the preset input value, at which point the other component concentrations were compared with the described input values. If they were not in agreement, the program was rerun with a corrected set of estimated feed outlet conditions. The area elements were added after each step to obtain the total membrane area requirements.

Different processes were considered for utilizing the recovered SO_2. These included various methods of preparing sulfur, sulfuric acid, and liquid SO_2. Only those processes which seemed to have the inherent advantage of being easily integrated with the rest of the membrane system were studied in detail.

Because of the major contributions to SO_2 emissions from the combustion of fossil fuels for power generation (46% of the total SO_2 emissions in the U.S., according to a 1966 U.S.D.H.E.W. estimate), first consideration was given to the applicability of a membrane system to recover the SO_2 from power plant stack gases. The systems detailed generally above were evaluated, and several variations of each process scheme were considered. Large- and medium-size power plants were investigated. The initial SO_2 content of the stack gases was assumed to be 0.2 v/o, and a design basis of 90% removal of the pollutant was used. The water vapor and CO_2 contents of the stack gas were assumed to be 6.0% and 14.5%, respectively. Whereas the membrane developed has a high permeability for SO_2, the membrane separation factors for SO_2/H_2O and SO_2/CO_2 are approximately 2.0 and 14.0, respectively. Thus, because of the unfavorable concentration ratios in the stack gas, coupled with the above separation factors, a high degree of concentration of the SO_2 in the permeate stream is not possible. Because of the low initial concentration of SO_2 in the stack gas (0.2%), the desired rate of removal (90%) and the high stack gas flow rate membrane area requirements were of the order of 7.5 to 8 million square feet for a 1000 MW power plant, for reasonable values of the total sweep flow rate and operating pressure conditions.

System analyses indicated that the use of turbine exhaust steam (at 1.5 inches Hg) as a sweeping medium for removing the permeating gases from the membrane interface would be the most economical system. Steam, at this pressure, would not permeate through the membrane in the reverse direction. Since only a small fraction of the plant steam consumption would be required for the membrane system [~2.4% of the total turbine requirements[8]], the capital and operating cost for producing the membrane package steam might be charged to the power plant itself rather than to the recovery operation.

The effort which must be expended for merely separating and concentrating the SO_2 (to a maximum of about 10%) was great. Table IV summarizes the cost data for the two plants considered. A membrane cost of $1/ft^2 was used, which amounted to about 25% of the total plant investment. A subsequent reaction

TABLE IV

Power Plant Operation

Plant Size	Plant Cost	Operating Cost
440 MW	$21.66 × 10^6 ($50.4/kW)	0.662 mil/kw-hr
1000 MW	$33.42 × 10^6 (33.4/kW)	0.447 mil/kw-hr

of the concentrated SO_2 with a hydrocarbon additive (based on a potential but commercially untried process developed by the now defunct Thiogen Co.) was assumed with the final product being sulfur. Credit is taken for the sulfur produced (at $40 per long ton). No other schemes were known which might be able to handle the low pressure, moist, and still relatively dilute gas stream. Labor costs were not included in the operating data. Because of the costs involved, and the uncertainty involved in the above reaction process, the power plant applications study was terminated, with the conclusion that the present membrane cannot be applied efficiently and effectively to the separation of SO_2 from the combustion gases.

Consideration was next given to gas effluents of higher SO_2 content and lower flows, such as are found in various ore-smelting operations (which account for about 12% of the SO_2 emissions in the U.S.). A range of SO_2 concentrations was considered (4.0% to 10.0%) and a total stack gas flow of about 20,000 SCFM was used as a basis. In this case, because of the low CO_2 and H_2O vapor contents of the stack gas (about 6.5% and 3.5%, respectively) a relatively efficient membrane separation could be performed. The most economical system was one in which a condensable, impermeable sweep vapor carried the permeating SO_2 from the membrane, with subsequent condensation of the entire sweep stream to produce liquid SO_2 as a salable product. Economic evaluations were prepared for both atmospheric and vacuum sweeping of the membrane system. For comparison purposes, a hydrocarbon (e.g., heptane) was considered as the sweeping medium,

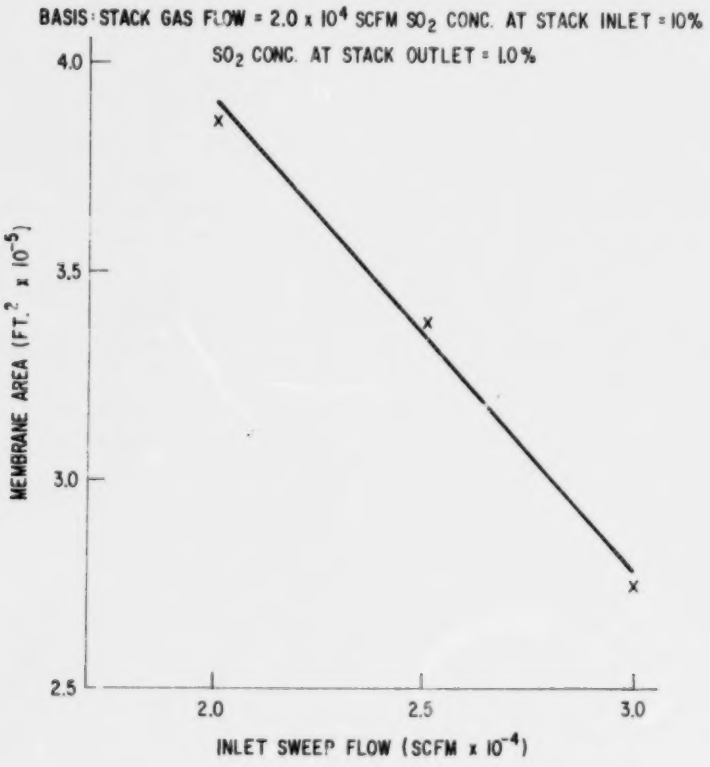


Fig. 4 Membrane area vs sweep flow (Smelter case).

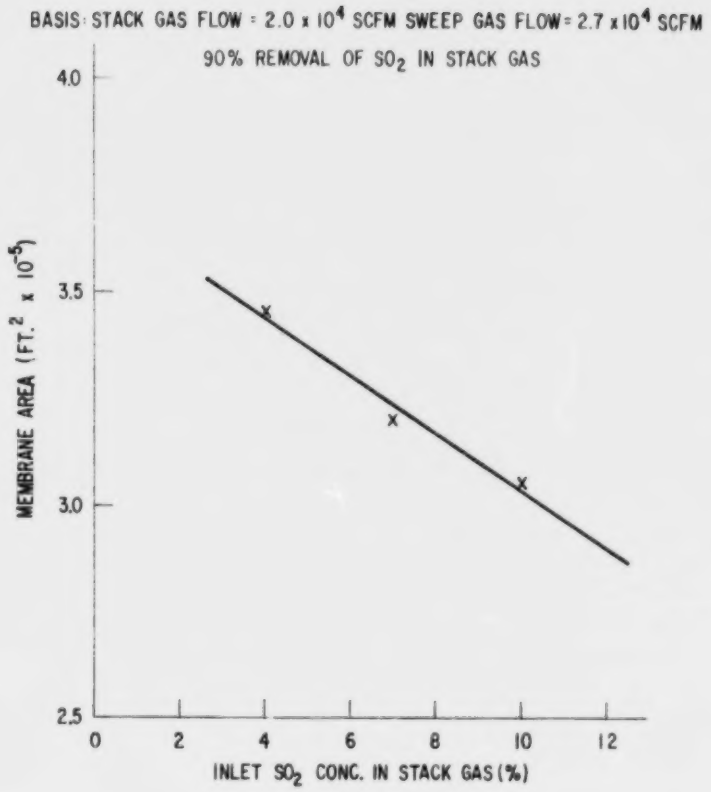


Fig. 5 Membrane area vs SO_2 concentration in stack gas (Smelter case).

since it could be used at both atmospheric and low pressures, and since it was believed that the nonpolar hydrocarbon would be essentially impermeable in the membrane. Marked economic advantages were found in both capital and operating costs for vacuum operation because of the lesser mass of sweep vapor which must be handled. This advantage is only partially offset by the additional compressors and power requirements needed for this type of operation. Figure 4 shows the relation of required membrane area to sweep gas flow rate for 90% removal of the SO_2 from a stack gas of 20,000 SCFM total flow and initial SO_2 concentration of 10%. Figure 5 shows the effect of initial SO_2 concentration on the required membrane area for 90% removal of the SO_2 from the inlet stack gas. If less removal were necessary at the lower inlet concentrations, less membrane area would be required. The over-all effect of this on the plant's actual costs would be determined as a balance with the required amount of sweep gas needed to efficiently perform the separation. The costs for separating and producing liquid SO_2 as a by-product were summarized in Table V. These costs assume no loss of sweep vapor as a result of reverse permeation through the membrane. [N.B.: The manufacturer's list price of liquid SO_2, based on tank-car lots, f.o.b., New York, in April 1968, is about 3.5¢/lb SO_2.[9]] Estimates of economically permissible vapor losses (assuming no restrictions due to pollution hazards) show the range of sweep vapor permeabilities to be 5 to 100 times less than that of O_2 or N_2, depending on the cost of the vapor. Thus, the sweep vapor must indeed be impermeable.

TABLE V

Smelter Operation to Produce Liquid SO_2

Stack SO_2 Concentration (%)	Sweep Pressure (atm)	Plant Cost ($)	Operating Cost ($)
10	1	1.458×10^6	0.492×10^6 (0.30 ¢/lb SO_2)
7	1	1.394×10^6	0.459×10^6 (0.46¢/lb SO_2)
4	1	1.383×10^6	0.443×10^6 (0.68¢/lb SO_2)
10	0.2	1.152×10^6	0.318×10^6 (0.22 ¢/lb SO_2)

Basis: 90% recovery of SO_2 from stack gas.
20,000 SCFM stack gas flow.

TABLE VI

Hydrocarbon Solubility in Polyethylene Glycol
(Union Carbide's Carbowax 4000)

Hydrocarbon	Solubility $\left(\frac{\text{Moles}}{\text{kg C-4000}} @ 1 \text{ atm HC Pressure}\right)$	
	T = 75°C	T = 100°C
Pentane	--	0.11
Hexane	0.38	.23
Heptane	.36	--
Cyclomethylhexane	.87	--
2-Heptene	.42	--
Freon 113	.16	--
FC-75 (3M fluorocarbon)	--	0.03
2-Chloroethanol	--	1.63 (may be in error)
Tetrahydropyran	--	0.61
CO_2	.027	.017
SO_2	1.34	.55

A search for a sweep vapor to be used in treating gases from ore-smelting operations was made. Since at the time of this study the membrane backing became wet when a pressure difference was applied, atmospheric pressure operation was assumed. This put very stringent requirements on the physical properties of the vapor, and a suitable one has not yet been found. The vapors considered were listed in Table VI together with their solubilities. With the renewed possibility of vacuum operation, many new vapors may be tried, and it may yet be possible to find a sufficiently impermeable hydrocarbon vapor for use in the membrane system.

Alternatively, one can use water vapor as the sweep vapor at a pressure approximately equal to the partial pressure of water in the gas to be cleaned. This pressure can be adjusted to a convenient range by humidifying the stack gas prior to SO_2 removal. This may be done as a by-product of scrubbing the gas to remove dust and SO_3.

Due to the high permeability of the membrane to water vapor, the vapor may pass through the membrane in either direction depending on the local gradient in vapor pressure. However, water has the great advantage of being low in cost and nonpolluting. Therefore, the low-pressure steam sweeping approach appears to be the most promising one available at present. The cost of producing by-product SO_2 in this manner should not be very different from the costs as shown in Table V. A schematic diagram of such a system is shown in Fig. 6. Experiments on low-pressure steam sweeping are in progress in connection with another application of membranes and will yield operational experience with this approach.

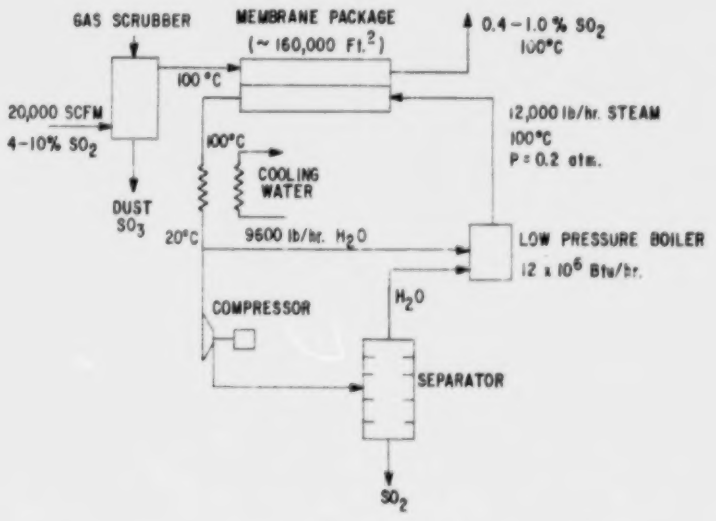


Fig. 6 Smelter system schematic.

The fact that hydrocarbons have the high solubilities in polyethylene glycol as shown in Table VI suggests that they should have permeabilities about equal to that of SO_2. This offers the interesting possibility of using this membrane to remove hydrocarbon vapors from air or other impermeable gases. A number of pollution control applications of this possibility are obvious, such as cleaning air laden with solvent vapors.

CONCLUSIONS

A number of conclusions from this work can now be made. The immobilized liquid membrane which has been developed is substantially more permeable to and selective for SO_2 than any other membrane. It is usable for extended periods at temperatures up to 100°C. Because the SO_2/CO_2 separation factor is not substantially higher than 10 to 15, this membrane is not suitable for removing SO_2 from combustion gases. However, with the new advance making possible a membrane which will not break through under a pressure difference, it appears that a commercially attractive system might be developed which would be applicable for treating gases typical of those produced in ore-smelting operations.

RECOMMENDATIONS

The preliminary system's analyses show that an economically attractive system for removing SO_2 from smelter effluents may be available if the liquid membrane can withstand a pressure difference. Thus, the work of Meldon should be continued with the goal of producing a thin, immobilized liquid film with the same flux as the present 3μ film. A multilayer membrane package should then be attempted. Current costs of the Solvinert backing are extremely high; thus a cheaper method of supporting the membrane must be found. The Celanese Celgard porous polypropylene may be a possible backing material.

ACKNOWLEDGEMENT

The authors wish to acknowledge many helpful discussions and key suggestions of P. H. Kydd and E. E. Bostick.

REFERENCES

1. W. Robb et al., U.S. Patent 3, 335, 545.

2. W. Ward and W. Robb, Science, 156, 1481 (1967).

3. Solvinert filters are a class of solvent-resistant microporous membranes manufactured by Millipore Corp., Bedford, Mass.

4. Chemical Engineering Cost Files, 1958 to present.

5. M. Peters, Plant Design and Economics for Chemical Engineers, McGraw-Hill Book Co., Inc., New York (1958).

6. C. H Chilton, ed., Cost Engineering in the Process Industries, McGraw-Hill Book Co., Inc., New York (1960).

7. H. C. Bauman, Fundamentals of Cost Engineering in the Chemical Industry, Reinhold Publishing Corp., New York (1964).

8. Mechanical Engineer's Handbook, 6th ed.

9. Oil, Paint, and Drug Reporter (April 1968).

APPENDIX A

BIBLIOGRAPHY OF SO_2-HYDROCARBON REACTION SYSTEM

A1. H. J. Backer and J. A. Bottema, "Addition de Sulfite au Dimethylbutadiene," Rec. Trav. Chim., 51, 294 (1932).

A2. H. J. Backer, J. Strating, and C. M. H. Kool, "Quelques Sulfones Cycliques, Formées par Addition D'Anhydride Sulfureux à Des Butadienes," Rev. Trav. Chim., 58, 778 (1939).

A3. F. S. Dainton and K. J. Ivin, "The Photochemical Formation of Sulphinic Acids from Sulphur Dioxide and Hydrocarbons," Trans. Faraday Soc., 46, 374 (1950).

A4. F. S. Dainton and K. J. Ivin, "The Kinetics of the Photochemical Gas-Phase Reactions Between Sulphur Dioxide and n-Butane and 1-Butene Respectively," Trans. Faraday Soc., 46, 382 (1950).

A5. F. S. Dainton and K. J. Ivin, "The Kinetics of Polysulfone Formation. I. The Formation of 1-Butene Polysulfone at 25°C," Proc. Roy. Soc., A212, 96 (1952).

A6. F. S. Dainton and K. J. Ivin, "The Kinetics of Polysulfone Formation. II. The Formation of 1-Butene Polysulfone in the Region of the Ceiling Temperature," ibid., p. 207.

A7. A. H. Frazer, "Thermal Stability of the Copolymer of SO_2 and cis, cis-1, 5-cyclooctadiene," J. Polymer Sci., A2, 4031 (1964).

A8. D. S. Frederick, H. D. Cogan, and C. S. Marvel, "The Reaction Between SO_2 and Olefins. I. Cyclohexene," J. Am. Chem. Soc., 56, 1815 (1934).

A9. M. Hunt and C. S. Marvel, "The Reaction Between SO_2 and Olefins. II. Propylene," J. Am. Chem. Soc., 59, 1691 (1935).

A10. C. S Marvel and L. H. Dunlap, "Vinyl Chloride Polysulfone," J. Am. Chem. Soc., 61, 2709 (1939).

A11. C. S. Marvel and W. W. Williams, "Acetylene Polysulfones. XI. The Compound $C_{10}H_{16}SO_2$ from 1-Pentynepolysulfone and Some Experiments on Other Acetylene Polysulfones," ibid., p. 2710.

A12. C. S. Marvel and W. W. Williams, "Polysulfones. XII. The Synthesis of 3, 4- and 2, 5-Di-n-propyltetrahydrothiophene-1, 1-dioxides," ibid., p. 2714.

A13. L. L. Ryden, F. J. Glavis, and C. S. Marvel, "Reaction Between SO_2 and Olefins and Acetylenes. VI. Ascaridole as a Catalyst for the Reaction," J. Am. Chem. Soc., 59, 1014 (1937).

A14. L. L. Ryden and C. S. Marvel, "Polysulfones from Acetylene and SO_2," J. Am. Chem. Soc., 58, 2047 (1936).

A15. W. F. Seyer and E. G. King, "Systems of Sulfur Dioxide and Hydrogen Derivatives of Benzene," J. Am. Chem. Soc., 55, 3140 (1933).

A16. H. Staudinger, French Patent 698, 857, July 11, 1930.

A17. H. Staudinger and B. Ritzenthaler, "Uber hochpolymere Verbundungen, 104. Mitteil.: Uber die Anlagerung von Schwefeldioxyd an Athylen-Derivate," Ber., 458 (1935).

A18. C. Walling, Free Radicals in Solution, John Wiley and Sons, Inc., New York (1957).

APPENDIX B

Breakdown of Smelter Operation Cost*

A. Capital Cost Summary	A	B	C	D
Major Equipment				
Heat Exchangers	$163,000	$157,600	$152,600	$134,900
Compressor, drive	21,000	15,000	11,000	10,000
Boiler	77,000	77,000	77,000	77,000
Separator	9,000	9,000	9,000	9,000
Drying Tower	10,000	10,000	10,000	10,000
	280,000	268,600	259,600	240,900
Total Investment (≈ 4.0 x Equipment Cost)	$1,120,000	$1,074,400	$1,038,400	$ 963,600
Membrane Cost (@ $1/ft^2)	338,000	320,500	345,000	189,000
Total Plant Investment	$1,458,000	$1,394,900	$1,383,400	$1,152,600
B. Operating Cost Summary				
Raw Materials				
Fuel	92,400	92,400	92,400	13,400
Water	96,400	92,700	90,000	27,500
Power	70,300	51,100	39,500	94,000
Depreciation (≈ 14% of TPI)	204,000	195,100	193,600	161,000
Taxes & Insurance (≈ 2% of TPI)	29,200	27,900	27,600	23,000
Total Operating (not including labor)	492,300	459,200	443,100	318,900
Cost (¢/lb SO_2)	0.30	0.46	0.63	0.22

* Basis: 20,000 SCFM in stack gas -- ≈ 27,000 SCFM in sweep gas for cases A, B, C
90% removal of initial stack SO_2

Case A: 10% initial SO_2 concentration
Case B: 7% initial SO_2 concentration
Case C: 4% initial SO_2 concentration
Case D: 10% initial SO_2 concentration; Sweep pressure = 0.2 atm